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Photoabsorption cross section of negatively charged alkali-metal clusters

J. M. Pacheco*
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany
and Neils Bohr Institute, Blegdamsvej 17, DK-2100, Copenhagen Ø, Denmark

W. Ekardt
Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, D-1000 Berlin 33, Germany

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The optical response of anionic clusters of sodium and potassium with up to 40 valence electrons is calculated making use of a self-interaction-corrected linear-response formalism recently developed by the authors. It is found that, for these systems, the surface plasmon is excited systematically above the ionization threshold and is strongly Landau damped, with its strength distribution spread over an energy interval of typically ≈1 eV, reflecting the shorter lifetime of these systems with respect to the neutral and cationic clusters. Furthermore, it is found that temperature-dependent broadening mechanisms are able to wash out the fine structure in the line shapes of the cross sections.

The time-dependent local-density approximation (TDLDA) developed in 1980 by Zangwill and Soven,[1] constitutes framework used in computing the optical properties of metal clusters.[2] TDLDA is a linear-response theory which incorporates, in a self-consistent way, the electronic screening of an external, eventually time-dependent, perturbation which couples to the electronic density. Because of the LDA inherent to this formalism, the electrons moving in the mean-field potential interact spuriously with themselves. This well-known feature of the LDA leads to sizable errors in the case of systems such as atoms, molecules, and clusters. Among other shortcomings, LDA is clearly unable to provide stable solutions for the ground state (GS) of commonly observed negative ions.[4,5] To the self-interaction errors present at the LDA GS level, TDLDA introduces an additional one. Indeed, in the presence of an external perturbation the TDLDA potential felt by one electron, which is the sum of the external perturbing potential and the screening potential, receives a screening contribution due to all the electrons, including itself, which leads to a wrong overestimation of screening.

To the best of our knowledge, and among the different approaches used to compute the optical properties of clusters, only the different formulations of Ref. 6 and the Hartree-Fock random-phase-approximation (HF-RPA) calculations of Ref. 7 are completely free of the self-interaction problem described above. Unfortunately, the computational load of the methods of Ref. 6 is such that they can be applied, at present, to clusters with few atomic constituents.[6] On the other hand, the exchange-only HF GS description of metallic clusters[7] means that HF-RPA leads to little improvement as compared to the simpler TDLDA results.

Besides the methods of Refs. 6 and 7, other approaches have been considered[8,9,3] which are based on the empirical evidence that the self-interaction corrections (SIC) (Ref. 10) improve[10,11] the LDA description of the GS of many-electron systems. Indeed, since the SIC lacks a first-principles justification, it remains an open problem to what extent the SIC-LDA eigenvalues are good representations of the quasiparticle energies. An attempt to clarify this point was carried out in Ref. 12, where the quasiparticle energies were computed in the spirit of Hedin's GW approximation.[13] Even though there is no fundamental justification as to whether the GW approximation is able to provide good quasiparticle energies,[14,15] the good agreement obtained between the SIC-LDA results and the GW-like eigenvalues is noteworthy.[3,12]

The extension of these SIC methods to the calculation of the dynamical properties of many-electron systems benefits (suffers) from the same first-principles results[16] (questions), concerning its validity, as the TDLDA itself. In the SIC approaches, the self-interaction problem is not completely cured, due to the nonlinear character of the exchange-correlation (XC) functionals used in the LDA. Furthermore, of Refs. 8, 9, and 3, only in Ref. 3 have the self-interaction corrections been consistently included, to linear order, in the screening term, the method being known as FULL-SIC-TDLDA. In the other attempts, the problem of self-polarization of the electron was either neglected,[9] or dealt with in *ad hoc* way,[8] with sizable consequences for the calculated dynamical properties (cf. the discussion in Ref. 3).

FULL-SIC-TDLDA has been applied to the study of the optical response of neutral *and* cationic metal clusters.[3] These calculations, in which use has been made of the jellium model, are parameter free in the sense that the Wigner-Seitz radius r_s of the metal has been always fixed to its bulk value (this is not only a common practice in calculations of this type, but also the only reasonable thing to do in the absence of any more physical input). As a result, the best overall agreement between theory and available experimental data has been obtained so far. Since the above-mentioned framework allows us to compute, in a natural way, the GS and excitation states of negatively charged (anionic) many-electron systems, we present, in this paper, nontrivial predictions for the static polarizabilities and photoabsorption cross sections of anionic alkali-metal clusters.[17] Because of its relevance,[18] we shall consider clusters of sodium and potassium and will present results for clusters spanning a size range up to 40 valence electrons. For computational convenience we concentrate on the so-called "magic" clusters, corresponding to completely filled shells of valence electrons, thereby using the spherical jellium background model to replace the discrete ionic structure. We shall start with a short review of the FULL-SIC-TDLDA formalism, proceeding with the discussion of the results obtained and ending this paper with a summary and conclusions.[19]

The description of the GS of a cluster with $\mathcal{N}$ ions and N valence electrons, in the SIC-LDA (Ref. 10) to XC, amounts to solving, self-consistently, the set of Kohn-Sham-like equations with a SIC orbital-dependent potential,

$$\left[\frac{-\hbar^2}{2m}\Delta+V^{(i)}_{\mathrm{SIC}}(\mathbf{r})\right]\psi^{(i)}_j(\mathbf{r})=\epsilon^{(i)}_j\psi^{(i)}_j(\mathbf{r}) , \tag{1}$$

where $V^{(i)}_{\mathrm{SIC}}$ reads

$$V^{(i)}_{\mathrm{SIC}}(\mathbf{r})=V_I(\mathbf{r})+e^2\int\frac{[n(\mathbf{r}_1)-n^{(i)}(\mathbf{r}_1)]d\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}+V_{\mathrm{xc}}[n(\mathbf{r})]-V_{\mathrm{xc}}[n^{(i)}(\mathbf{r})] . \tag{2}$$

$V_I(\mathbf{r})$ is the jellium potential of $\mathcal{N}$ ions, $\psi^{(i)}_j(\mathbf{r})$ represents the eigenfunction of orbital potential $V^{(i)}_{\mathrm{SIC}}$ with quantum numbers j, and $\epsilon^{(i)}_j$ is the corresponding eigenvalue. Furthermore, the densities are defined as

$$n(\mathbf{r})=\sum_{i=1}^{N} n^{(i)}(\mathbf{r})=\sum_{i=1}^{N}|\psi^{(i)}_i(\mathbf{r})|^2 . \tag{3}$$

V_{xc} is the XC potential of Gunnarsson and Lundqvist.[20] Because of the orbital dependence of the SIC potentials, we overcome the nonorthogonality problem of the single-particle wave functions by orthonormalizing them (using the Gram-Schmidt method) at each step of the self-consistent iteration scheme.

Under the action of an external, time-dependent perturbation of the form

$$V_{\mathrm{ext}}(\mathbf{r})=-r^l P_l(\cos\theta)\cos(\omega t) , \tag{4}$$

the valence electrons will react by screening the external field. In FULL-SIC-TDLDA, the screening potential reads[3]

$$V^{(i)}_{\mathrm{screen}}(\mathbf{r},\omega)=e^2\int\frac{[\delta n(\mathbf{r}_1,\omega)-\delta n^{(i)}(\mathbf{r}_1,\omega)]d\mathbf{r}_1}{|\mathbf{r}-\mathbf{r}_1|}+\frac{\delta V_{\mathrm{xc}}[n(\mathbf{r})]}{\delta n}[\delta n(\mathbf{r},\omega)-\delta n^{(i)}(\mathbf{r},\omega)] , \tag{5}$$

where $\delta n^{(i)}(\mathbf{r})$ are the orbital contributions to the total SIC screened induced density

$$\delta n(\mathbf{r},\omega)=\sum_{i}^{\mathrm{occ}}\delta n^{(i)}(\mathbf{r},\omega) . \tag{6}$$

This form of the screening potential is the one which is consistent with the SIC performed in the GS calculation, and which involves only linear changes in the density, as required by the formalism we are using.

The effect of the screening potential is then included by requiring self-consistency between the induced density and the total perturbing potential. This leads to the FULL-SIC-TDLDA system of coupled equations (for details, cf. Ref. 3),

$$\delta n^{(i)}(\mathbf{r},\omega)=\int d\mathbf{r}_1\Lambda^{(i)}(\mathbf{r},\mathbf{r}_1,\omega)[V_{\mathrm{ext}}(\mathbf{r}_1,\omega)+V^{(i)}_{\mathrm{screen}}(\mathbf{r}_1,\omega)] . \tag{7}$$

In Eq. (7), $\Lambda^{(i)}$ represents the contribution of occupied orbital (i) to the independent-particle susceptibility, which can be written in terms of the SIC orbital-dependent Green's functions[3,9] as

$$\Lambda^{(i)}(\mathbf{r},\mathbf{r}_1,\omega)=[\psi^{(i)*}_i(\mathbf{r})\psi^{(i)}_i(\mathbf{r}_1)G^{(i)}(\mathbf{r},\mathbf{r}_1,\epsilon^{(i)}_i+\hbar\omega)+\mathrm{c.c.}(\omega\rightarrow-\omega)] . \tag{8}$$

Due to the spherical geometry of our clusters, with closed-shell structure, the response is diagonal in angular momentum, and the polarizability of multipolarity l is related to the l component $\delta n_l(r,\omega)$ by

$$\alpha_l(\omega)=-e^2\frac{4\pi}{2l+1}\int_0^{+\infty}dr\, r^{l+2}\delta n_l(r,\omega) . \tag{9}$$

The photoabsorption cross section is simply given in terms of the imaginary part of α by $\sigma(\omega)=(4\pi\omega/c)\,\mathrm{Im}[\alpha_{l=1}(\omega)]$.

In Table I, numerical values for the static polarizabilities [$l=1,\omega=0$ in Eq. (9)] are given, in units of the classical polarizability of a conducting metallic sphere of radius $R_0=r_sN^{1/3}$, where r_s is the bulk Wigner-Seitz radius

TABLE I. Static polarizabilities of anionic clusters of sodium (Na$^-$) and potassium (K$^-$), as well as of neutral (Na) and cationic (Na$^+$) clusters of sodium, with 8, 20, and 40 valence electrons, in units of $R_0^3=Nr_s^3$ (where N is the number of valence electrons) and calculated with FULL-SIC-TDLDA. The numerical values for the anionic clusters correspond to the results of the present calculation, whereas the other values were taken from Ref. 3.

	8	20	40
K$^-$	2.14	1.84	1.58
Na$^-$	2.35	1.92	1.67
Na	1.70	1.61	1.51
Na$^+$	1.46	1.45	1.41

of the alkali metal. For the sake of comparison, we also tabulate the results[3] for neutral and cationic sodium clusters containing the same number of valence electrons (8, 20, and 40).

Several features emerge from Table I. In particular, one can observe that, for a given N, the static polarizabilities are largest for the anions. This can be understood classically by recalling that the polarizability scales with the volume of the sphere. Since the net confining electrostatic force that the ions exert on the electrons is smallest for the anions, this implies that the valence electrons in the anions span a larger volume than the ones in their neutral and cationic partners. Furthermore, the deviations from the classical results have been rationalized[21] in terms of the so-called "spill-out" of the electronic charge density with respect to the sharp jellium edge. Since the bulk density of sodium ($r_s = 4$) is higher than the one of potassium ($r_s = 4.86$), for a fixed N and ionization state one expects the "spill-out" to be larger in sodium than in potassium, which in turn explains why the values in Table I are systematically larger for sodium than for potassium. The larger spill-out for sodium was in fact confirmed by calculating the quantity $\delta = (4\pi)/N \int_{R_0}^{+\infty} n(r) r^2 / dr$, which provides information on the amount of electronic charge located outside of the sharp jellium edge. This feature was found to be independent of the size and ionization state. Finally, the largest deviations from the classical value observed for the anionic species lead one to expect (from, e.g., the simple plasmon-pole relation between the static polarizability and the energy position of the surface plasmon) that the surface plasmon is further redshifted in these species as compared to, e.g., the neutral partners. This feature is not clearly observed (compare, e.g., Fig. 1 of present paper and Figs. 1–3 of Ref. 3) due to the sizable amount of Landau damping taking place in the anionic species, which leads to a large overall linewidth spanning an energy interval larger than the one corresponding to the above-mentioned redshift.

The dynamic response of the sodium and potassium clusters is shown in Fig. 1. Vertical arrows indicate the ionization threshold. In sharp contrast to their neutral and cationic partners, the anions have most of their strength located in an energy region above this threshold.[22] Therefore, a coupling between the surface plasmon and this continuum of single electronic excitations takes place, leading to the detachment of an electron from the cluster after the excitation of the plasmon via absorption of one photon. This mechanism is entirely analogous to the coupling known, in the theory of the electron gas at finite temperature, as Landau damping. It is also observed in the giant resonances in atomic nuclei, in which case it is strongly size dependent, a feature which seems to emerge as well from the results of the present calculation, where we observe strong Landau damping for the eight valence electron systems (leading to flat and smooth line shapes), and which becomes progressively reduced as the number of valence electrons increases. It is a true damping mechanism and is distinct from the Landau fragmentation commonly observed in the neutral and cationic clusters, which is a pure quantum size effect (QSE) with no implications for the lifetime of the clusters. Indeed, we would like to point out that the width of the peaks displayed in Fig. 1 has two different origins. As can be seen from the peaks located at energies below the ionization threshold, the width is very small, and corresponds exactly to the 10 meV of intrinsic width that was input for the numerical solution of the Green's function (for details of the numerical procedure, cf. e.g., Ref. 3). This is included for numerical convenience and, therefore, has *no* physical significance. On the other hand, at energies higher than the threshold mentioned above, the peaks display widths which can be much larger than the input intrinsic width of 10 meV. This width is due to the true coupling between the (in this case) surface plasmon and the continuum of electronic unbound excitations. The (outgoing-wave) boundary conditions imposed on the solution of the Green's functions ensure that the unbound electrons do leave the system. Therefore, the resulting width of the peaks is directly related to the probability of an electron to leave the cluster.

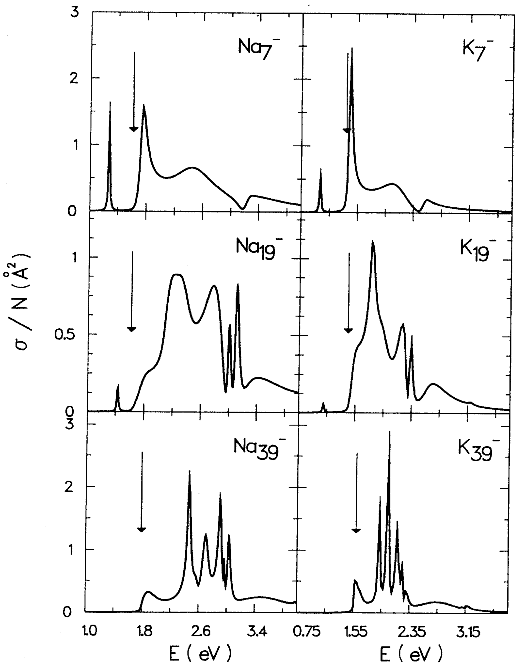

FIG. 1. Line shapes of the photoabsorption cross section per valence electron for Na_7^-, K_7^-, Na_{19}^-, K_{19}^-, Na_{39}^-, and K_{39}^-. The arrows indicate the ionization threshold for each cluster.

The damping nature associated with this coupling can be best illustrated in a time-dependent picture as done, e.g., in Ref. 23, in the context of the damping of the giant monopole resonance (GMR) in the atomic nucleus ^{16}O due to (in this case) nucleon detachment, and in the framework of the time-dependent Hartree-Fock (TDHF) approximation. Indeed, also in this case (for a system ~6 orders of magnitude smaller than a microcluster and with energies ~6 orders of magnitude larger), the collective nuclear breathing mode (GMR) of ^{16}O is embedded in a continuum of single nucleon excitations, and Landau damping leads now to the attenuation in time of the amplitude of the monopole oscillations (cf. e.g., Fig. 3 in Ref. 23). This attenuation is directly related (via Fourier transform) to the linewidth of the strength function (cf., e.g., Fig. 1 in Ref. 23).

Finally, we would like to point out that, from Fig. 1, it is clear that the overall linewidths (Δ) and centroid energies ($\bar{E}$) associated with the dynamical response of the potassium clusters are systematically lower than the ones associated with their sodium partners (this is also true for the case of neutral and positively charged clusters). These overall features can be obtained making use of the sum-rule approach,[24,25] which provides estimates for these quantities. However, while these can be written in closed form using the spill-out charge δ and the static polarizabilities as inputs, they are unable to provide any information on the detailed features of the dynamical response.

We would like to discuss now the effect of the internal temperature of the clusters in the results obtained so far. The formulation utilized in this paper does not incorporate the following mechanisms, which can effectively contribute to modify the line shape (and linewidth):

(1) Perturbations originating from the discrete structure of the ionic background and which are disregarded in the jellium approach.

(2) The presence of other broadening mechanisms, such as the ones discussed at length in Refs. 26, 27, and 28 and which have the net effect of smoothing the line shapes presented in Fig. 1.

Little is known about the effect of the first type of process. Still, one can expect that these effects are somewhat minimized in the anionic species due to the imbalance of positive and negative charge, which favors the electronic dominance in determining the geometrical arrangement of the ions. On the other hand, the second class of processes can act to wash out the structures obtained at the level of linear response, a feature which depends on the vibrational temperature of the cluster. To illustrate this point further, we show, in Fig. 2, the result of including the broadening mechanisms discussed in Refs. 26 and 28 at different temperatures, in the response of K_{19}^-. To this end, we used the numerical results of Ref. 28 and folded the line shape of Fig. 1 with normalized Lorentzian functions with widths in accord with these results. Since the results of Ref. 28 were obtained for the cation, we expect them to somewhat underestimate the broadening effects in the anion. One can then observe that, already for temperatures of ≈ 300 K, these mechanisms act to produce smooth line shapes.

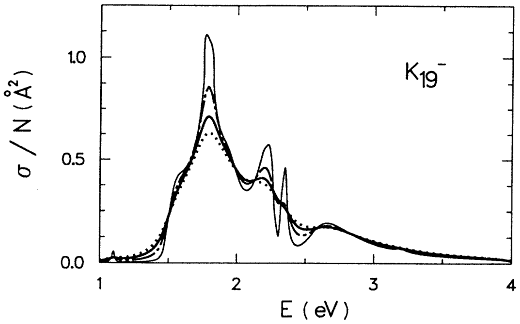

FIG. 2. Line shapes of the photoabsorption cross section per valence electron for K_{19}^-. The FULL-SIC-TDLDA line shape is drawn, for reference, with a thin full curve. The broadening mechanisms discussed in Ref. 28 were included for three different temperatures: 100 K (chain-dashed line), 300 K (thick full line), and 500 K (dotted line). Already at ≈ 300 K, these mechanisms act to wash out most of the structure present in the FULL-SIC-TDLDA line shape.

To summarize, the surface plasmon excited on an anionic alkali-metal cluster occurs at energies above the ionization threshold.[29] This is markedly different from the plasmon excitations in neutral and positively charged clusters, and leads to novel features which strongly affect the response of these systems to light. At the level calculated here, the cross sections for photoabsorption span broad (≈ 1-eV) energy intervals, with line shapes which are less pronounced and less structured than the corresponding ones associated with photoabsorption in neutral and cationic species. This in turn reflects the shorter lifetime of these systems, due to the competing process of electron detachment. The amount of Landau damping is found to decrease with the cluster size, at least within the size range covered in the present paper (a feature which is, however, expected to be preserved for larger clusters). As expected, the centroid of the strength distribution is progressively blueshifted as the cluster size increases. Other relaxation mechanisms, which depend on the vibrational temperature of the clusters, may be able to wash out the detailed structures present in microscopic approaches such as the one carried out in the present paper.

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[*] Permanent address: Departamento de Fisica da Universidade, 3000 Coimbra, Portugal.

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[17] We would like to point out that, although the LDA provides a stable solution for some negatively charged clusters, the resulting mean-field potential develops an artificial Coulomb barrier, decreasing to zero as $+1/r$, which is manifestly unphysical.

[18] Experimental measurements of the photoabsorption cross section of anionic clusters, though unavailable at present, are planned to be carried out in the near future (see Ref. 19).

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[29] We would like to point out that these conclusions apply within the size range considered. Indeed, preliminary results indicate that, with increasing cluster size, the mean energy of the surface plasmon in anionic clusters progressively approaches the ionization threshold, eventually crossing it.